

WE CLAIM:

1. A method of making a phosphono-substituted dipyrromethane, comprising:
reacting an aldehyde or acetal having at least one phosphono group substituted thereon with pyrrole to produce a phosphono-substituted dipyrromethane;
and wherein said phosphono is selected from the group consisting of dialkyl phosphono, diaryl phosphono, and dialkylaryl phosphono.
2. The method of claim 1, wherein said aldehyde or acetal is coupled to said at least one phosphono group by a linking group
- 10 3. The method of claim 2, wherein said linking group is selected from the group consisting of aryl, alkyl, alkylaryl, and alkylarylalkyl groups.
- 15 4. The method of claim 1, wherein said aldehyde or acetal has three phosphono groups substituted thereon.
5. A method of making a phosphono substituted dipyrromethane, comprising:
reacting a halo-substituted dipyrromethane with a phosphite to produce a phosphono-substituted dipyrromethane;
20 wherein said phosphite is selected from the group consisting of dialkyl phosphites, diaryl phosphites, and dialkylaryl phosphites;
and wherein said phosphono is selected from the group consisting of dialkyl phosphono, diaryl phosphono, and dialkylaryl phosphono.
- 25 6. The method of claim 5, wherein said halo is coupled to said dipyrromethane by a linking group, said linking group selected from the group consisting of alkyl, aryl, alkylaryl, and alkylarylalkyl groups.
- 30 7. The method of claim 5, wherein said halo is selected from the group consisting of chloro, bromo and iodo.

8. A 5-phosphonodipyrromethane, wherein said phosphono is selected from the group consisting of dialkyl phosphono, diaryl phosphono, and dialkylaryl phosphono.

5 9. The 5-phosphonodipyrromethane according to claim 8, wherein said phosphono is coupled to said dipyrromethane by a linking group.

10 10. The 5-phosphonodipyrromethane according to claim 9, wherein said linking group is selected from the group consisting of alkyl, aryl, alkylaryl, and alkylarylalkyl groups.

11. A method of making a 5-phosphono, 1-acyldipyrromethane, comprising: reacting a 5-phosphonodipyrromethane with a Grignard reagent to produce an intermediate compound; and then
15 reacting said intermediate compound with a Mukaiyama reagent to produce a 5-phosphono, 1-acyldipyrromethane.

12. The method of claim 11, wherein said 5-phosphono is selected from the group consisting of dialkyl phosphono, diaryl phosphono, and dialkylaryl phosphono.

20 13. The method of claim 12, wherein said phosphono is coupled to said dipyrromethane by a linking group.

14. The method of claim 13, wherein said linking group is selected from the group consisting of alkyl, aryl, alkylaryl, and alkylarylalkyl groups.

25 15. A dipyrromethane selected from the group consisting of (a) 1-phosphonoacyldipyrromethanes, and (b) 5-phosphono, 1-acyldipyrromethanes.

30 16. The compound of claim 15, wherein said 5-phosphono is selected from the group consisting of dialkyl phosphono, diaryl phosphono, and dialkylaryl phosphono group.

17. The compound of claim 15, wherein said compound is a 5-phosphono, 1-acyldipyrromethane and said 1-acyl group is a 1-phosphonoacyl group.

18. A method of making a 9-halo, 5-phosphono, 1-acyldipyrromethane,
5 comprising:

halogenating a 5-phosphono, 1-acyldipyrromethane to produce a 9-halo, 5-phosphono, 1-acyldipyrromethane; wherein said phosphono is selected from the group consisting of dialkyl phosphono, diaryl phosphono, and dialkylaryl phosphono.

10 19. The method of claim 18, wherein said halo is selected from the group consisting of chloro, bromo and iodo.

20. The method of claim 18, wherein said phosphono is coupled to said dipyrromethane by a linking group.

15 21. The method of claim 20, wherein said linking group is selected from the group consisting of alkyl, aryl, alkylaryl, and alkylaryalkyl groups.

22. A 9-halo, 5-phosphono, 1-acyldipyrromethane compound wherein said
20 phosphono is selected from the group consisting of dialkyl phosphono, diaryl phosphono, and dialkylaryl phosphono.

23. The compound of claim 22, wherein said halo is selected from the group consisting of chloro, bromo and iodo.

25 24. The compound of claim 22, wherein said phosphono is coupled to said dipyrromethane by a linking group.

25. A method of making a chlorin, comprising:
30 reducing a 9-halo, 5-phosphono, 1-acyldipyrromethane to produce a first reaction product; and then

reacting said first reaction product with a western half to produce said chlorin; wherein said phosphono is selected from the group consisting of dialkyl phosphono, diaryl phosphono, and dialkylaryl phosphono.

5 26. The method of claim 25, wherein said halo is selected from the group consisting of chloro, bromo and iodo.

27. The method of claim 25, wherein said phosphono is coupled to said dipyrromethane by a linking group.

10 28. The method of claim 27, wherein said linking group is selected from the group ~~consisting of~~ alkyl, aryl, alkylaryl, and alkylaryalkyl groups.

15 29. A chlorin having a phosphono group coupled thereto at the 5 position, the 10 position, or both the 5 and 10 position.

30. The chlorin of claim 29, wherein said phosphono is coupled to said chlorin by a linking group, said linking group is selected from the group consisting of alkyl, aryl, alkylaryl, and alkylaryalkyl groups.

20 31. The chlorin of claim 29, wherein said phosphono is selected from the group consisting of dialkyl phosphono, diaryl phosphono, and dialkylaryl phosphono

25 32. A chlorin of claim 29 having a phosphono group coupled thereto at both the 5 and 10 position.

33. A method of making a porphyrin substituted at the 5 position with at least one phosphono group, comprising:

30 reacting a 5-phosphono-substituted dipyrromethane with a dipyrromethane-dicarbinol to produce said porphyrin; wherein said phosphono is selected from the group consisting of dialkyl phosphono, diaryl phosphono, and dialkylaryl phosphono.

34. The method of claim 33, wherein said phosphono is coupled to said dipyrromethane by a linking group, said linking group selected from the group consisting of alkyl, aryl, alkylaryl, and alkylaryalkyl groups.

5 35. The method of claim 33, wherein said at least one phosphono group consists of three phosphono groups.

36. A porphyrin substituted at the 5 position and the 10 position with a phosphono group.

10 37. A method of making a substituted porphyrin compound, comprising:
reacting a halo-substituted porphyrin with a phosphite or a salt thereof to produce a porphyrin having a phosphono group coupled thereto;
wherein said phosphite is selected from the group consisting of dialkyl phosphite, diaryl phosphite, dialkylaryl phosphite, trialkyl phosphite, triaryl phosphite, and trialkylaryl phosphite;
and wherein said phosphono is selected from the group consisting of dialkyl phosphono, diaryl phosphono, and dialkylaryl phosphono.

20 38. The method of claim 37, wherein said halo-substituted porphyrin comprises a porphyrin having a halo group coupled thereto by an intermediate linking group.

25 39. The method of claim 37, wherein said linking group is selected from the group consisting of alkyl, aryl, alkylaryl, and alkylaryalkyl groups.

40. The method of claim 37, wherein said porphyrin comprises a member of a double-decker or triple-decker sandwich coordination compound.

30 41. The method of claim 37, further comprising the step of metalating said porphyrin having a phosphono group coupled thereto.

42. A method of making a phosphonoic acid-substituted porphyrin or chlorin, comprising:

reacting a porphyrin or chlorin having a protected phosphono group substituted thereon at the 5 position with a trialkysilyl halide and a base in a solvent to
5 produce a porphyrin or chlorin having a phosphonic acid group substituted thereon.

43. The method of claim 42, wherein said trialkylsilylhalide is selected from the group consisting of trimethylsilyl chloride and trimethylsilyl bromide.

10 44. The method of claim 42, wherein said base is a tertiary amine.

45. The method of claim 42, wherein said base is a trialkylamine.

15 46. The method of claim 42, wherein said phosphono is coupled to said porphyrin or chlorin with an intermediate linking group.

47. The method of claim 42, wherein said intermediate linking group is selected from the group consisting of alkyl, aryl, alkylaryl, and alkylarylalkyl groups.

20 48. The method of claim 42, wherein said porphyrin or chlorin is a porphyrin, and wherein said porphyrin comprises a member of a double-decker or triple-decker sandwich coordination compound.

49. A method of making coupled porphyrins, comprising:

25 reacting (i) a first porphyrin substituted with a halo or ethyne group and a protected phosphono group with (ii) a second porphyrin having an ethyne or halo group in a Sonogashira reaction to couple said first and second porphyrins;

wherein said first porphyrin is substituted with halo when said second porphyrin is substituted with ethyne, and said first porphyrin is substituted with ethyne when said second porphyrin is substituted with halo.
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50. The method of claim 49, wherein at least one of said first and second porphyrins comprises a member of a double-decker or triple-decker sandwich coordination compound.